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ANSTO Samples - 1-week Report

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Disclaimer

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Australian Nuclear Science & Technology Organization (ANSTO)
Interdicted Samples

1-Week Report

Laboratory: Lawrence Livermore National Laboratory (United States of America)

Current Status: Categorization is complete and characterization is well underway. Samples FSC-11-3-1 (NSR-F-270409-01) and FSC-11-3-2 (NSR-F-270409-02) are depleted uranium powders of moderate purity (~71-80 % U). Both were depleted to ~0.41-0.44% ^{235}U. Both samples have easily detectable amounts of ^{236}U, as well as ^{232}U at low levels. Samples FSC-11-3-1 and FSC-11-3-2 appear to be tails from an enrichment facility that used reprocessed U as part of its feed-stock. The U isotopic compositions of the two samples, while similar, differ outside of analytical uncertainty, suggesting that these samples came from different lots of material. Sample FSC-11-3-3 is indistinguishable from a natural uranium ore concentrate (~78% U) of moderate purity. Two anomalous objects (11-3-1-4 and 11-3-2-5) were found in the material during aliquoting, but have not been further analyzed.

Potential Issues: None.

Sample Identification

ANSTO Identifier	Mass	LLNL Identifier
NSR-F-270409-01	5.00 g	FSC-11-3-1
NSR-F-270409-02	5.00 g	FSC-11-3-2
NSR-F-130503	10.02 g	FSC-11-3-3

Accomplishments since the 24-Hour Report

- Gamma spectrometry analysis with a longer counting time
- Loss-on-heating analysis
- Uranium isotopic analysis by multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS)
- Uranium assay by isotope dilution mass spectrometry (IDMS)
- Analysis of trace elemental impurities by quadrupole inductively coupled plasma-mass spectrometry (ICP-MS)
- Age-dating analysis using the ^{234}U/^{230}Th chronometer by multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS)

Main Analyses Remaining

- Pu analysis by multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS)
- Alpha spectrometry for ^{232}U and ^{238}Pu (if appropriate)

- Isotopic analysis of Pb, Nd, and Sr
- Stable isotope analysis (C, N, O, S)
- Optical microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) for powder characterization
- Further analysis of vis/NIR spectra
- Organic analysis of samples by semi-permeable membrane extraction (SPME)
- X-ray diffraction (XRD) analysis for chemical composition
- Further analysis of anomalous objects FSC-11-3-1-4 and FSC-11-3-2-5.

Gamma spectrometry analysis with a longer counting time

In order to reduce the detection limits for some of the fission product and activation species from those reported in the 24-hour report, we re-counted the gamma spectrometry sub-samples for 3 days. The analytical results are presented in Table 1.

Table 1.
Gamma Spectrometry Results from 3-Day Count

Sample Ratio	11-3-1-3	11-3-2-3	11-3-3-3
gU / gram	0.689 +/- 5%	0.740 +/- 5%	0.749 +/- 5%
235U/238U	4.59e-3 +/- 1.6%	4.03e-3 +/- 1.6%	7.27e-3 +/- 1.8%
234U/238U	3.02e-5 +/- 6.7%	2.57e-5 +/-5.8%	5.65e-5 +/- 3.6%
232U/238U	< 5e-10	< 3e-10	< 1.8e-10
232Th/238U	< 1.2e-4	< 2.4e-4	< 9e-5
228Th/238U	5.52e-14 +/- 7.1%	3.39e-14 +/- 9.5%	<5e-15
226Ra/238U	4.35e-12 +/- 68%	1.06e-11 +/- 40%	1.64e-11 +/- 12%
239Pu/238U	< 3e-6	< 2e-6	< 1.6e-6
237Np/238U	< 1.2e-8	< 1.5e-8	< 6e-9
40K/238U	8.5e-5 +/- 12%	< 8e-6	5.4e-6 +/- 76%
54Mn/238U	< 1.2e-15	< 1.2e-15	< 6e-16
60Co/238U	< 6e-15	< 6e-15	< 4e-15
106Ru/238U	< 1.8e-14	< 2.2e-14	< 1.1e-14
125Sb/238U	< 4e-14	< 5e-14	< 3e-14
137Cs/238U	< 6e-14	< 8e-14	< 4e-14
144Ce/238U	< 1.0e-13	< 1.2e-13	< 6e-14
152Eu/238U	< 7e-14	< 7e-14	< 5e-14
182Ta/238U	< 4e-15	< 3e-15	< 1.5e-15

Uranium Isotopic Analysis by Multi-collector Inductively Coupled Plasma-Mass Spectrometry (MC-ICP-MS)

Sub-samples "2-A" from each sample were dried (for loss-on-heating), then dissolved. Secondary gravimetric dilutions of each sample were spiked with ^{233}U, diluted in a 2% nitric acid solution, and analyzed on a Nu Plasma HR MC-ICP-MS. The U isotopic results, obtained on dilutions of the primary solution by MC-ICP-MS, are summarized in Table 3. Samples FSC-11-3-1 and FSC-11-3-2 were clearly depleted to ~0.41-0.44%. Both samples also have easily detectable amounts of ^{236}U. However, the U isotopic compositions of the two samples differ outside of analytical uncertainty. Sample FSC-11-3-3 is consistent with natural U.

Table 2.
U Isotopic Results
Expressed as ratios to 238U (top) and as atomic percents (bottom)

	Atomic Ratios					
Sample ID	**234U/238U**	**exp. uncert.**	**235U/238U**	**exp. uncert.**	**236U/238U**	**exp. uncert.**
FSC 11-3-1-2-A	0.00002768	0.00000018	0.0044439	0.0000087	0.00002312	0.00000012
FSC 11-3-2-2-A	0.00002509	0.00000015	0.0040974	0.0000081	0.00007711	0.00000039
FSC 11-3-3-2-A	0.00005485	0.00000033	0.007250	0.000015	<10E-8	----

	Atomic Percent					
Sample ID	**234U**	**exp. uncert.**	**235U**	**exp. uncert.**	**236U**	**exp. uncert.**
FSC 11-3-1-2-A	0.002756	0.000018	0.44240	0.00087	0.002302	0.000012
FSC 11-3-2-2-A	0.002499	0.000015	0.40803	0.00081	0.007679	0.000039
FSC 11-3-3-2-A	0.005445	0.000033	0.7197	0.0015	<10E-8	----

Expanded uncertainties use a coverage factor of three (k=3).

Uranium assay by isotope dilution mass spectrometry (IDMS)

The U assay data from analysis of the ^{233}U spiked sample are summarized in Table 3. All samples are of moderate purity. (For comparison, the U assay for pure U_3O_8 would be 84.8%; for pure UO_2 is 88%.)

Table 3.
Results of U Assay Analysis

on a dry weight basis	
Total U g U / g-sample	Expanded Uncert. (k=3)
0.7085	0.0027
0.7988	0.0037
0.7782	0.0033

Loss-on-heating Analysis

Sub-samples "2-A," intended for isotope ratio analysis, were dried at 140 °C for two hours. The masses of the samples were measured before and after heating to determine loss-on-heating, which should represent the moisture content of the samples. The analytical results are presented in Table 4.

Table 4.
Loss-on-Heating (% Moisture) Results

Sample ID	LOH (% Moisture)	Expanded Uncert. (k=3)
FSC-11-3-1-2-A	1.14	0.12
FSC-11-3-2-2-A	6.00	0.30
FSC-11-3-3-2-A	3.12	0.20

Analysis of Trace Elemental Impurities by Quadrupole ICP-MS (Q-ICP-MS)

The "2-B" sub-samples, intended for trace elemental analysis, were diluted in a HNO_3/HF solution to U concentrations of ~180 ppma and were then analyzed on a Thermo Electron X7 Quadrupole Inductively Coupled Mass Spectrometer. An internal standard corrects for instrument drift and suppression from the uranium matrix. The results are summarized in Table 5. Concentrations are shown in micrograms/gram of sample (as received, not dried), along with preliminary uncertainties (GUM compliant uncertainties to follow). The Sn results highlighted in orange indicate where the duplicate analyses do not agree within the expected analytical uncertainty. This sort of disagreement usually indicates sample heterogeneity, but could also indicate contamination at some stage of sampling and analysis. We are currently investigating the Sn results, as well as re-analyzing-ran a few elements in collision-cell mode which can lower detection limits for elements such as As, Se and confirm Fe etc.

Table 5.

Results of Trace Impurity Analysis

		FSC11-3-1-2-B		FSC11-3-2-2-B		FSC11-3-3-2-B	
		n=3	stdev	n=2	stdev	n=2	stdev
Be	ug/g samp	< 0.01	---	< 0.01	---	< 0.01	---
Na	ug/g samp	91	3	41	4	78.1	1.1
Mg	ug/g samp	10.5	0.6	29.8	0.4	16.2	1
Al	ug/g samp	24.7	1.5	19.3	1.7	82	20
K	ug/g samp	67000	3000	< 100	---	< 100	---
Ca	ug/g samp	119	13	58.3	1.1	213	4
Ti	ug/g samp	4.3	0.3	1.49	0.15	2.4	0.3
V	ug/g samp	1.2	0.06	< 0.04	---	0.11	0.02
Cr	ug/g samp	30.2	0.9	5.496	0.008	0.51	0.02
Mn	ug/g samp	16.8	0.4	1.07	0.11	79.6	2
Fe	ug/g samp	445	17	55.4	1.4	321	10
Co	ug/g samp	2.73	0.13	0.31	0.02	0.247	0.011
Ni	ug/g samp	19.5	0.6	4.5	0.4	< 1	---
Cu	ug/g samp	16.8	0.6	6.3	0.9	0.42	0.02
Zn	ug/g samp	9.3	0.4	0.9	0.05	6.89	0.2
Ga	ug/g samp	< 0.2	---	< 0.2	---	< 0.2	---
Ge	ug/g samp	< 0.2	---	< 0.2	---	< 0.2	---
As	ug/g samp	0.83	0.17	< 0.05	---	0.59	0.07
Se	ug/g samp	9.3	0.6	<0.3	---	<0.3	---
Rb	ug/g samp	9.8	0.3	0.188	0.006	0.22	0.05
Sr	ug/g samp	6.6	0.3	0.622	0.013	1.3	0.05
Y	ug/g samp	0.03	0.007	< 0.01	---	0.145	0.004
Zr	ug/g samp	1.48	0.05	0.3147	0.0005	439	10
Nb	ug/g samp	0.25	0.04	<0.003	---	<0.003	---
Mo	ug/g samp	1.63	0.03	0.037	0.008	2.79	0.08
Ru	ug/g samp	< 0.02	---	< 0.02	---	< 0.02	---
Rh	ug/g samp	< 0.001	---	< 0.001	---	< 0.001	---
Pd	ug/g samp	< 0.015	---	< 0.015	---	< 0.015	---
Ag	ug/g samp	< 0.015	---	0.2	0.008	0.91	0.04
Cd	ug/g samp	26.2	0.8	< 0.05	---	0.3	0.05
Sn	ug/g samp	14	0.6	0.769	0.005	3	4
Sb	ug/g samp	0.6	0.1	<0.05	---	<0.05	---
Te	ug/g samp	2.89	0.08	< 0.2	---	< 0.2	---
Cs	ug/g samp	0.41	0.05	0.225	0.005	0.2	0.013
Ba	ug/g samp	36.9	1.3	8	0.3	6.57	0.11

		FSC11-3-1-2-B		FSC11-3-2-2-B		FSC11-3-3-2-B	
		n=3	stdev	n=2	stdev	n=2	stdev
La	ug/g samp	0.58	0.03	< 0.05	---	20.9	0.4
Ce	ug/g samp	1.11	0.04	< 0.02	---	34	0.7
Pr	ug/g samp	0.0154	0.0011	< 0.005	---	2.89	0.04
Nd	ug/g samp	0.065	0.004	< 0.01	---	7.15	0.15
Sm	ug/g samp	< 0.02	---	< 0.02	---	0.413	0.003
Eu	ug/g samp	< 0.005	---	< 0.005	---	0.04	0.003
Gd	ug/g samp	0.0141	0.0011	< 0.005	---	0.531	0.007
Tb	ug/g samp	< 0.002	---	< 0.002	---	0.0217	0.0007
Dy	ug/g samp	< 0.005	---	< 0.005	---	0.0371	0.0014
Ho	ug/g samp	< 0.002	---	< 0.002	---	0.0054	0.0003
Er	ug/g samp	< 0.005	---	< 0.005	---	0.013	0.003
Tm	ug/g samp	< 0.002	---	< 0.002	---	< 0.002	---
Yb	ug/g samp	< 0.005	---	< 0.005	---	0.00885	0.00007
Lu	ug/g samp	<0.001	---	<0.001	---	<0.001	---
Hf	ug/g samp	<0.02	---	<0.02	---	0.134	0.013
Ta	ug/g samp	<0.002	---	<0.002	---	<0.002	---
W	ug/g samp	6	0.5	< 0.1	---	1.78	0.06
Re	ug/g samp	< 0.01	---	< 0.01	---	< 0.01	---
Ir	ug/g samp	< 0.005	---	< 0.005	---	< 0.005	---
Pt	ug/g samp	< 0.005	---	< 0.005	---	< 0.005	---
Tl	ug/g samp	1.01	0.04	< 0.01	---	< 0.01	---
Pb	ug/g samp	18.02	0.07	47.7	0.5	6.3	0.2
Th*	ug/g samp	0.0452	0.0011	0.00698	0.00018	9.105	0.099

*Th results from IDMS analysis (see Table 8 below)

Age-dating analysis using the $^{234}U/^{230}Th$ chronometer

Fractions of sub-samples "2-A" were spiked with ^{229}Th and the Th was separated, purified and measured by MC-ICPMS. The concentrations of ^{230}Th relative to ^{234}U (from the uranium analysis) were used to calculate model ages (see Table 6), based upon the assumption that all Th was removed from the sample at some point and that the material remained a closed system afterwards (no loss or addition of Th). From these results, Samples FSC-11-3-1 and FSC-11-3-2 yield anomalously old ages -- either due to incomplete removal of Th during purification or subsequent contamination by natural thorium.

From these IDMS analyses, one also obtains the Th concentrations in the sample (Table 7) and the $^{230}Th/^{232}Th$ ratio (Table 8). For natural uranium ore concentrates like FSC-11-3-3, the $^{230}Th/^{232}Th$ atom ratio will be useful in identifying the source of the U ore, but only with a suitable database.

Table 6.
Model Ages Calculated from ^{230}Th and ^{234}U Concentrations

		years before Reference Date				
Sample ID	Reference Date	230Th-234U Model Age (years)	combined std. uncert.	expanded uncert. (k=3)	Model Date	Expanded Uncertainty (days)
FSC 11-3-1-2-A	28-Jan-11	75.27	0.66	1.98	20-Oct-35	723
FSC 11-3-2-2-A	28-Jan-11	47.89	0.42	1.27	9-Mar-63	464
FSC 11-3-3-2-A	28-Jan-11	47.03	0.21	0.64	17-Jan-64	233

Table 7.

Th Concentration (as measured by IDMS)

Sample ID	Th (ng/g)	expanded uncert. (k=3)
FSC 11-3-1-2-A	45.2	1.1
FSC 11-3-2-2-A	6.98	0.18
FSC 11-3-3-2-A	9015	99

Table 8.

Calculated $^{230}Th/^{232}Th$ Ratios from IDMS

	atomic ratio		Hypothetical 238U/232Th in Source	
Sample ID	230Th/232Th	uncert. (k=2)	238U/232Th	uncert. (k=2)
FSC 11-3-1-2-A	0.0890	0.0013	5250	77
FSC 11-3-2-2-A	0.3686	0.0059	21760	350
FSC 11-3-3-2-A	0.0006096	0.0000030	35.98	0.17

Technical Interpretation

Note: Technical interpretations are technical judgments based upon current results and will evolve as more results are obtained.

Categorization is complete and characterization is well underway.

FSC-11-3-1 (NSR-F-270409-01) and FSC-11-3-2 (NSR-F-270409-02)

Samples FSC-11-3-1 (NSR-F-270409-01) and FSC-11-3-2 (NSR-F-270409-02) are depleted uranium powders of moderate purity (~71-80 % U). Both were depleted to ~0.41-0.44% ^{235}U. Both samples have easily detectable amounts of ^{236}U and gamma spectrometry suggests the presence of ^{232}U at low levels. Therefore, the uranium feed stocks for 11-3-1 and 11-3-2 have both experienced a neutron flux. Other fission products, including ^{54}Mn, ^{60}Co, ^{106}Ru, ^{125}Sb, ^{137}Cs, ^{144}Ce, ^{152}Eu and ^{182}Ta, were below our detection limits. Samples FSC-11-3-1 and FSC-11-3-2 appear to be tails from an enrichment facility that used reprocessed U as part of its feed-stock.

Furthermore, the U isotopic compositions of the two samples, while similar, differ outside of analytical uncertainty, suggesting that these samples came from different lots of material.

Sample FSC-11-3-3

Sample FSC-11-3-3 is indistinguishable from a natural uranium ore concentrate (~78% U) of moderate purity.

Anomalous Objects

Two anomalous objects (11-3-1-4 and 11-3-2-5) were found in the material during aliquoting. These objects might be valuable for route attribution.